Understanding Silicone

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ABSTRACT: *Understanding silicones requires knowledge of the three operations used to make them: construction, functionalization and derivatization. These operations are explained and illustrated, respectively, with dimethicone, PEG-8 dimethicone and dimethicone copolyol silicone esters. In addition, structure-function relationships are explained.*

Silicone compounds have achieved outstanding growth in both the type and quantity used in the personal care area. In fact, there are few new cosmetic formulations in any market area today that do not contain silicone compounds. Despite this outstanding growth in acceptance, the structure-function relationship remains elusive to most of today's formulators. This is true even for many of the most technically sophisticated formulators.

Silicone polymers are a diverse class of compounds that encompass traditional silicone fluids, water-soluble polymers, oil-soluble polymers, fluoro-soluble polymers and polymers that have a range of solubility. They encompass a variety of forms from low-viscosity fluids to rubbery elastomers to resins. The problem is that the choice of compounds is overwhelming. With all these compounds and without a road map, the formulator will find it difficult to select an appropriate silicone for a specific application. The road map is known, but it is rather guarded by those who understand it. That road map is an understanding of the silicone technology and the structure-function relationship that exists within the technology base. That knowledge is no more complicated than the technology base used to make surfactants. While different, it is every bit as rich and flexible.

Silicone Technology

Silicone compounds have been known since the 1860s, but it was not until the pioneering of Eugene Rochow in the 1940s that this important class of compounds achieved commercial viability. This was due in large part to the development of a process called the *direct process* that now bears Rochow's name. Silicone chemistry provides the polymer chemist with the ability to construct precise molecules having desirable nanotechnology properties.

Silicone polymers are derived from quartz (SiO_2), a naturally occurring mineral that makes up 25% of the earth's crust. SiO_2 is converted to silicon (Si) at high temperature in the presence of a carbon source. **Figure 1** shows the two materials.

The resulting Si metal is then crushed and reacted in a fluidized bed reactor to produce chlorosilanes, using the Rochow process. The reaction is shown in **Figure 2** on page 96.

Chlorosilanes are manufactured by grinding up silicon metal and reacting it in a tubular reactor with methyl chloride. A small number of manufacturers perform this work. They are affectionately referred to as "crushers."

Figure 1. The transformation of quartz to silicon metal is the first step in making silicone compounds. Quartz is on the upper left and silicon on the lower right. (Photo by Thomas O'Lenick, copyright 2005, used by permission)

$$Si + CH_3Cl \longrightarrow (CH_3)_4\text{-}Si$$

$$(CH_3)_3\text{-}Si\text{-}Cl$$

$$(CH_3)_2\text{-}Si\text{-}(Cl)_2$$

$$CH_3\text{-}Si\text{-}(Cl)_3$$

$$Si\text{-}(Cl)_4$$

$$CH_3\text{-}SiH(Cl)_2$$

$$(CH_3)_2\text{-}SiHCl$$

Figure 2. Chlorosilane synthesis

Chlorosilanes are hydrolyzed in water to make intermediates used to make silicone derivatives. The reaction product of water and chlorosilanes is referred to as hydrolyzate.

The chlorosilanes are placed into water. HCl is stripped off. After distillation and a variety of clean-up processes, there emerges a series of silicone building blocks, the most important of which include hexamethyldisiloxane (MM), cyclomethicone (D4) and silanic hydrogen compound. That is just the start of the story.

These materials are combined in a variety of ways to make silicone polymers of interest. The types of reactions, called unit operations, include the following:

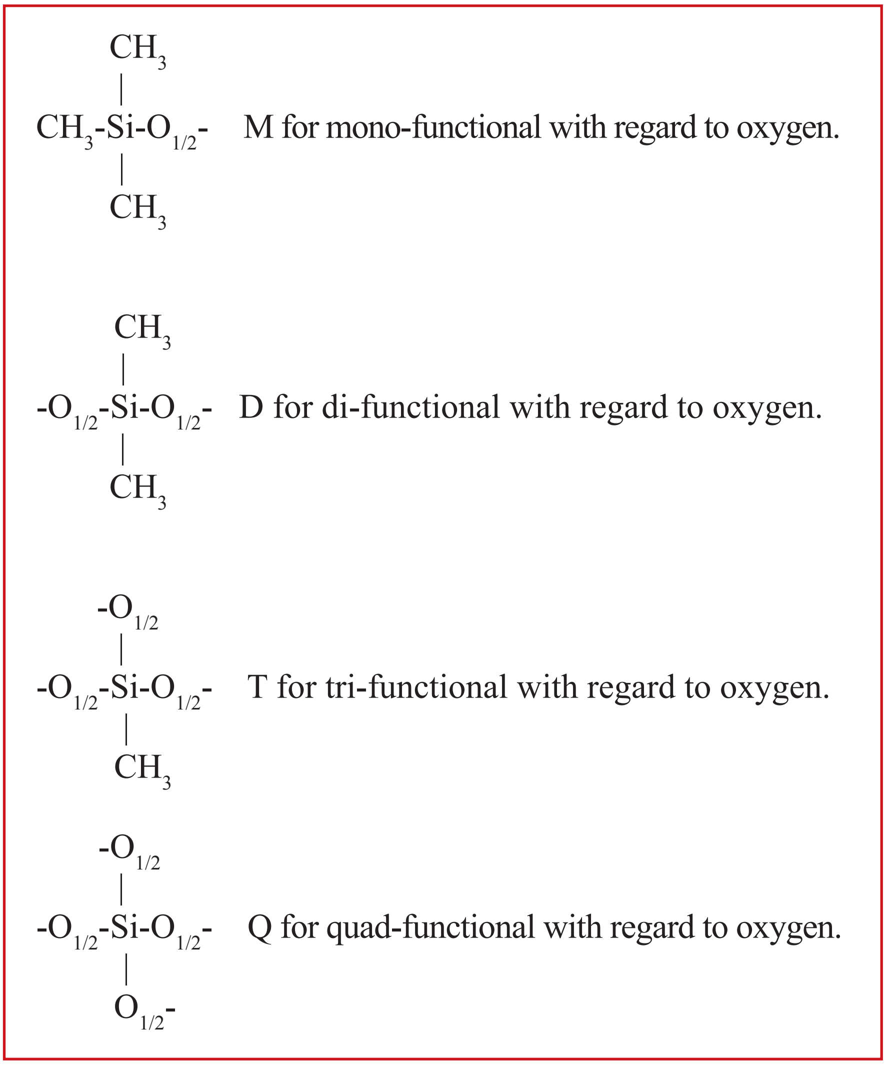
- Construction
- Functionalization
- Derivatization.

Construction

Highly specialized activities often create a jargon or language that speeds communication among its practitioners but also keeps people outside the field from feeling comfortable in these specialized activities. Chemistry, law and government are but a few examples.

Silicone chemistry is another example. The language of silicone chemistry makes use of the letters M, D, T and Q to specify structural groups placed into a molecule by its construction. The construction step is the process that determines the length of the polymer chain, its branching and its positions for insertion of organic groups. The shorthand for construction is shown in **Figure 3** on page 98.

Clearly, there are no real ½ O. This nomenclature is used so that when two or more groups are linked together a single oxygen exists between them. For example,



$$\begin{array}{rcl} & CH_3 & \\ & | & \\ CH_3\text{-} & Si & \text{-}O_{1/2}\text{-} \\ & | & \\ & CH_3 & \end{array}$$

M for mono-functional with regard to oxygen.

$$\begin{array}{rcl} & CH_3 & \\ & | & \\ \text{-}O_{1/2}\text{-} & Si & \text{-}O_{1/2}\text{-} \\ & | & \\ & CH_3 & \end{array}$$

D for di-functional with regard to oxygen.

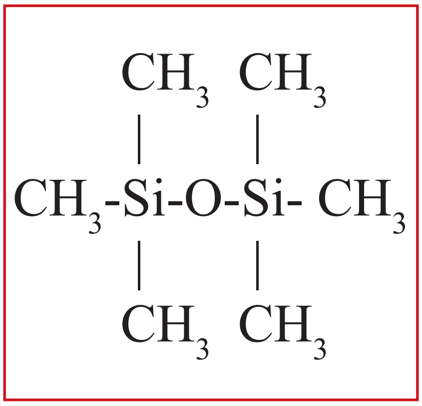
$$\begin{array}{rcl} & \text{-}O_{1/2} & \\ & | & \\ \text{-}O_{1/2}\text{-} & Si & \text{-}O_{1/2}\text{-} \\ & | & \\ & CH_3 & \end{array}$$

T for tri-functional with regard to oxygen.

$$\begin{array}{rcl} & \text{-}O_{1/2} & \\ & | & \\ \text{-}O_{1/2}\text{-} & Si & \text{-}O_{1/2}\text{-} \\ & | & \\ & O_{1/2}\text{-} & \end{array}$$

Q for quad-functional with regard to oxygen.

Figure 3. Shorthand for construction



$$\begin{array}{rcccl} & CH_3 & & CH_3 & \\ & | & & | & \\ CH_3\text{-} & Si & \text{-O-} & Si & \text{-}CH_3 \\ & | & & | & \\ & CH_3 & & CH_3 & \end{array}$$

Figure 4. MM (hexamethyldisiloxane)

the key material MM often is referred to as 0.65 viscosity silicone fluid or hexamethyl disiloxane. Its structure is shown in **Figure 4**. M units are chain terminators because they are mono-functional.

It would indeed be a sad situation if organo-functional materials were not available

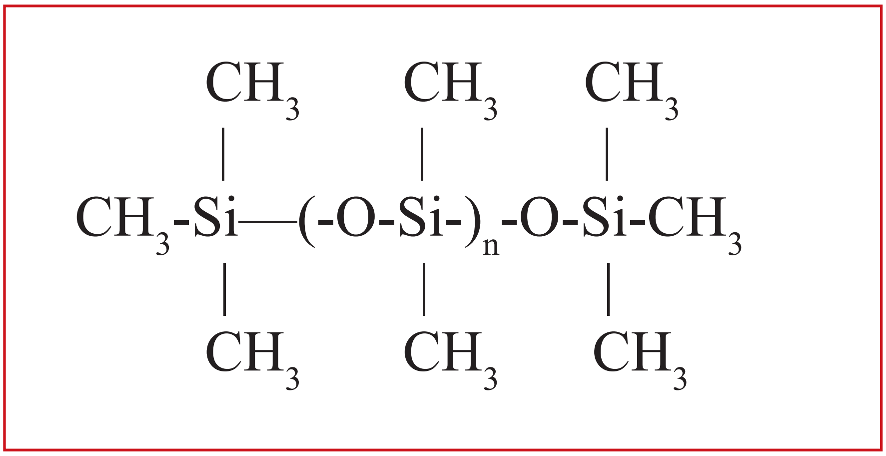
Dimethicone: To show the importance of construction, one needs only look at silicone fluids (dimethicone). Reaction of M and D will result in silicone fluids. An example is shown in **Figure 5**. D units are linear chain extenders. They provide larger and larger molecules having higher and higher viscosity. The correct name for the molecule in Figure 5 is MD80M.

Silicone fluids, also called silicone oils or simply silicones, are sold by their viscosity and range from 0.65 cst to 1,000,000 cst. If the product is not made by blending two fluids of different viscosities, the viscosity is related to molecular weight. The viscosity allows for an approximate calculation of the number of D units in the molecule, the so-called “n” value in the formula, as shown in **Table 1** on page 100. The differences in viscosity, feel and cushion going from a low-viscosity silicone fluid to one with a high-viscosity represent an important effect. This effect is strictly a function of construction.

Functionalization

Up to now this article has discussed only silicone homo-polymers. Of all the classes of silicone polymers, this class is best understood. This is an important class of compounds, but they represent only a small portion of all the compounds available to make products useful in the personal care market. It would indeed be a sad situation if the organo-functional materials were not available, or if the formulation chemist remained unaware of the advantages of such materials.

The preparation of a silanic-hydrogen-containing polymer by the construction process does not alter solubility. The silanic hydrogen pre-polymer assumes its altered

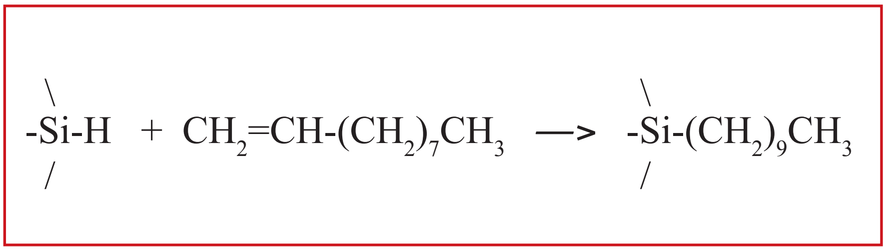


$$\begin{array}{rcccccl} & CH_3 & & CH_3 & & CH_3 & \\ & | & & | & & | & \\ CH_3\text{-} & Si & \text{—(-O-} & Si & \text{-)}_n\text{-O-} & Si & \text{-}CH_3 \\ & | & & | & & | & \\ & CH_3 & & CH_3 & & CH_3 & \end{array}$$

Figure 5. Dimethicone

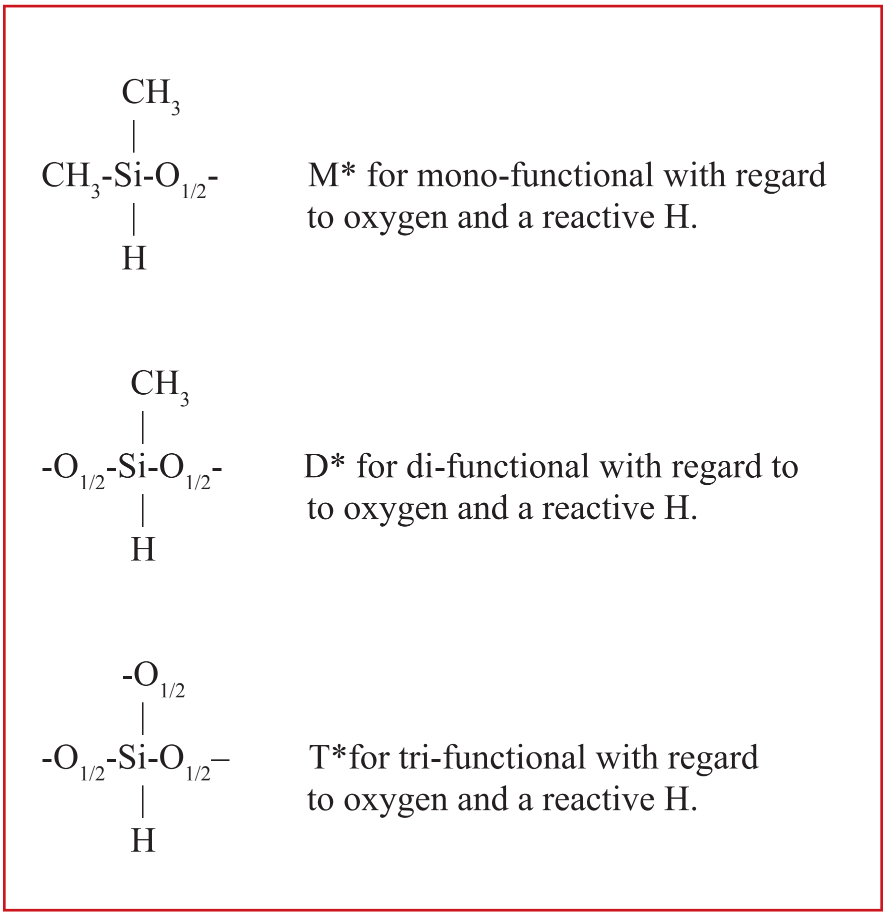
Table 1. Silicone fluids

Viscosity at 25°C (Centistokes)	Approximate Molecular Weight	Approximate "n" Value	Average Construction
5	800	9	MD_9M
50	3,780	53	$MD_{53}M$
100	6,000	85	$MD_{85}M$
200	9,430	127	$MD_{127}M$
350	13,650	185	$MD_{185}M$
500	17,350	230	$MD_{230}M$
1,000	28,000	375	$MD_{375}M$
10,000	67,700	910	$MD_{910}M$
60,000	116,500	1,570	$MD_{1570}M$
00,000	139,050	1,875	$MD_{1875}M$



$$\overset{\backslash}{\underset{/}{\text{-Si-H}}} + CH_2{=}CH\text{-}(CH_2)_7CH_3 \longrightarrow \overset{\backslash}{\underset{/}{\text{-Si-}}}(CH_2)_9CH_3$$

Figure 6. Reaction of silanic hydrogen with a terminal double bond to produce a stable Si-C bond



$$CH_3\text{-}\overset{CH_3}{\underset{H}{Si}}\text{-}O_{1/2}\text{-}$$

M* for mono-functional with regard to oxygen and a reactive H.

$$\text{-}O_{1/2}\text{-}\overset{CH_3}{\underset{H}{Si}}\text{-}O_{1/2}\text{-}$$

D* for di-functional with regard to to oxygen and a reactive H.

$$\text{-}O_{1/2}\text{-}\overset{\text{-}O_{1/2}}{\underset{H}{Si}}\text{-}O_{1/2}\text{–}$$

T*for tri-functional with regard to oxygen and a reactive H.

Figure 7. Shorthand for the construction of reactive compounds

solubility only after the functionalization reaction is run. For this reason silanic-hydrogen-containing polymers are considered precursors to organofunctional products. A single silanic hydrogen polymer can give rise to an entire family of analogs depending upon which functional group is placed onto the backbone in the functionalization reaction.

In order to make these products more easily formulated, organo-functional dimethicone compounds have been developed. These include alkyl dimethicone compounds that have improved oil solubility and PEG/PPG dimethicone compounds that have improved water solubility.

Another series contains compounds in which surfactant groups are grafted onto the backbone to improve virtually all surfactant properties, including detergency, conditioning, wetting and emulsification.

This ability to provide silicone products with improved applicability in personal care products opens the possibility of many high-performance products, but it also can be a source of frustration to many formulators who have not been given the necessary structure-function relationships to make intelligent choices in picking products. This author uses the term *formulator-friendly* to refer to properly selected silicone compounds.

Often the formulator is left to use products recommended by suppliers, rather than to participate in choosing the optimized product for an application. The key to avoid this situation is to learn the rules of structure-function related to silicones and apply them to new products, resulting in the most cost-effective products possible. This article reviews those important relationships and proposes compounds for consideration by the formulator.

The reaction used to place organofunctionality into silicone compounds is called hydrosilylation. This process is used in the construction part of silicone preparation.

The key reaction is one in which a silanic hydrogen (Si-H) is reacted with a terminal double bond. This results in a stable Si-C bond (**Figure 6**).

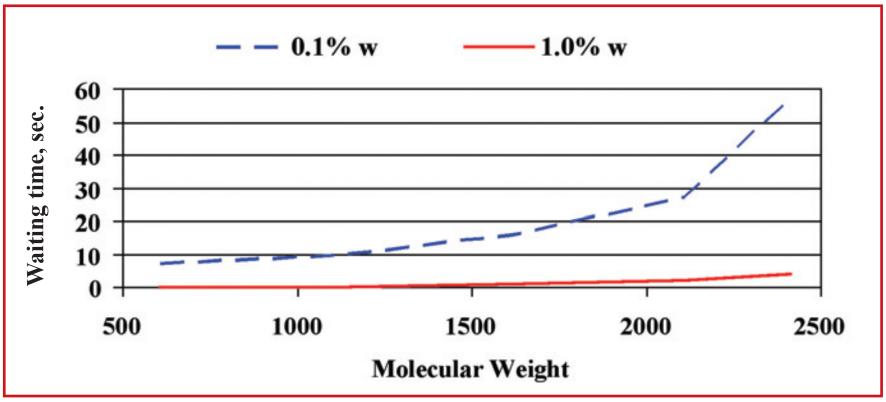


Figure 8. Draves wetting time

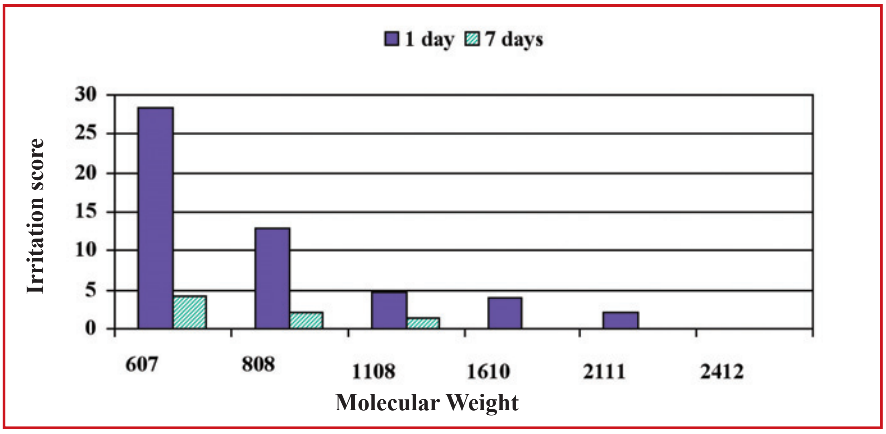


Figure 9. Eye irritation

Figure 7 shows the shorthand for the construction of a reactive compound. These materials are reacted within the equilibration reaction to make reactive intermediates that are hydrosilylated in the functionalization reaction. The vinyl-containing groups that are reacted include alpha olefin, allyl alcohol alkoxylates and fluoro vinyl compounds, whose formulas are shown, respectively, as follows:

CH_2=CH-$(CH_2)_7CH_3$
CH_2=CH-CH_2-$O(CH_2CH_2O)_8H$
CH_2=CH-CH_2 $(CF_2)CF_3$

The reaction of an Si-H-containing polymer with these alone or in combination results in several classes of products, where a class represents products with the same functional groups. The comparison of products within a class shows the importance of the construction.

PEG-8 dimethicone water-soluble silicone: The molecular weight of a PEG-8 dimethicone has a dramatic effect upon performance of the compound in terms of both wetting and irritation. Molecular weight is a measure of construction. **Figure 8** shows the molecular weight of molecules studied. Essentially, in the construction the compounds have the same ratio of D to D*, only higher numbers of both.

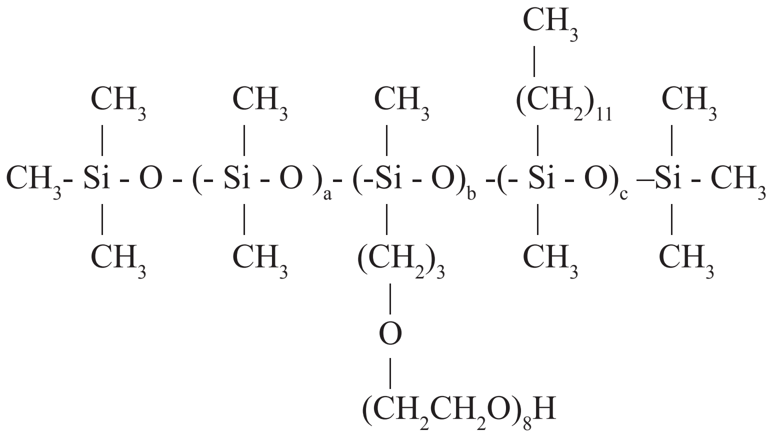
Wetting is an aspect of cosmetic formulation that is critical but often overlooked. When something is applied to the hair, skin, a pigment or any other surface, how that surface wets is critical to the usefulness of the formulation. A silicone wetting agent at low concentration (0.1–1.0% by weight) must be added to make the product function correctly. **Figure 8** details the Draves wetting time as a function of concentration. Draves wetting time is the time it takes to sink a cotton skein.

Construction also has a profound effect upon eye irritation, essentially disappearing at a molecular weight of 2412, as seen in **Figure 9**.

As the molecular weight increases, silicone compounds with the identical amount of PEG and the exact same ratio of D to D* undergo a transformation from wetting agents to emulsifiers to conditioners to water-proofing agents.

Table 2. Solubility of a series of alkyl dimethicone copolyol emulsifier compounds in selected fluids (S=Soluble, I=Insoluble, D=Dispersible)

Compound	Water	IPA	Mineral Spirits	Mineral Oil	Aromatic Solvent	Cyclic Silicone	Silicone Fluid
J208-212 at 1%	S	S	I	D	S	D	D
J208-212 at 10%	S	S	I	D	S	D	D
J208-412 at 1%	D	S	D	D	S	D	D
J208-412 at 10%	D	S	D	D	S	D	D
J208-612 at 1%	I	S	S	S	S	D	D
J208-612 at 10%	I	S	S	D	S	D	D
J208-812 at 1%	I	S	S	S	S	S	D
J208-812 at 10%	I	S	S	S	S	S	D



$$CH_3\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O\text{-}(\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}O)_a\text{-}(\text{-}\underset{(CH_2)_3O(CH_2CH_2O)_8H}{\overset{CH_3}{Si}}\text{-}O)_b\text{-}(\text{-}\underset{CH_3}{\overset{CH_3(CH_2)_{11}}{Si}}\text{-}O)_c\text{-}\underset{CH_3}{\overset{CH_3}{Si}}\text{-}CH_3$$

Figure 10. Alkyl dimethicone copolyol

This metamorphosis is driven by the lowest free energy of the molecule in solution. This is related in turn to the ease with which rotation occurs around the molecule backbone.

Alkyl dimethicone copolyol as emulsifiers: Illustrative of the importance of functionalization is a series of emulsifiers that are designed to be effective in preparing both water-continuous and water-discontinuous types of emulsions. This refers specifically to the alkyl dimethicone copolyol polymers conforming to the structure in **Figure 10** on page 104.

The compounds all have the same construction but differ in the number of alkyl-soluble and water-soluble groups. That means the values of "b" and "c" in **Figure 10** on page 104 are different but "b" + "c" is constant. This allows for a study of the effects of functionalization on a standard construction.

The products in this series have been designed to have different solubility in a variety of solvents (see **Table 2** on page 104). Additionally, the amount of alkyl in the molecule is reported using the 3D HLB[1,2] system, because it is much more descriptive than the standard HLB. The composition of the products is disclosed in **Table 3**.

Table 3. Composition of a series of alkyl dimethicone copolyol emulsifier compounds

Compound	EO (%)	Alkyl (%)	3D HLB x	3D HLB y
J208-212	48	6	9.6	1.2
J208-412	39	13	7.8	2.6
J208-612	28	22	5.6	4.4
J208-812	16	32	3.2	6.4

Petrolatum emulsions: Petrolatum emulsions are of interest in many areas. They have outstanding feel on the skin.

One study examined the effects of varying the ratios of petrolatum to oil. The most effective emulsifier in the series studied for petrolatum was J208-612. It appears that it can handle a wide range of petrolatum:water ratios. Varying the ratio of petrolatum to water results in products with very different properties. With **Formula 1**, for example, A is a very heavy lotion with an outstanding skin feel, B is a thin lotion with a cooling effect on the skin, and C is a heavy cream with the texture and feel of petrolatum. The technology can be expanded to cover many other oils, including the iso-alkanes and esters.

Formula 1. Petrolatum emulsions with varying ratios of petrolatum to oil

	A % wt	B % wt	C % wt
Modified hydroxyethylcellulose (Polysurf 67 CS, Hercules)	0.50	0.75	0.25
Tetrasodium EDTA (Versene 100, Dow)	0.40	0.40	0.40
Water *(aqua)*	48.90	70.65	25.00
Propylene glycol	2.00	2.00	
Lauryl PEG-8 dimethicone (Silsurf J208-612, Siltech)	4.00	4.00	4.00
Petrolatum	44.00	22.00	70.15
Propylparaben	0.20	0.20	0.20
	100.00	100.00	100.00

Another study examined the effects of varying the emulsifier. Formula 1 was repeated in **Formula 2,** adjusted to investigate the effect of the other emulsifiers in this silicone surfactant series[a].

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[a] *Silsurf is a registered trademark of Siltech LLC.*

Formula 2. Petrolatum emulsions with varying levels of emulsifier

	A % wt	B % wt	C % wt	D % wt
Modified hydroxyethylcellulose (Polysurf 67 CS, Hercules)	0.50	0.50	0.50	0.50
Tetrasodium EDTA (Versene 100, Dow)	0.40	0.40	0.40	0.40
Water *(aqua)*	48.90	48.90	48.90	48.90
Propylene Glycol	2.00	2.00	2.00	2.00
Lauryl PEG-8 dimethicone (Silsurf J208-612, Siltech)	4.00			
Lauryl PEG-8 dimethicone (Silsurf J208-612, Siltech)		4.00		
Lauryl PEG-8 dimethicone (Silsurf J208-612, Siltech)			4.00	
Lauryl PEG-8 dimethicone (Silsurf J208-612, Siltech)				4.00
Petrolatum	44.00	44.00	44.00	44.00
Propylparaben	0.20	0.20	0.20	0.20
	100.00	100.00	100.00	100.00

Table 4. Derivatization reactions of dimethicone copolyol as the raw material

Unit Operation on Dimethicone Copolyol	End Product
Esterification	Silicone Ester
Phosphation	Silicone Phosphate
Chloroalkylation	Silicone Quat
Carboxylation	Silicone Carboxylate
Sulfation	Silicone Sulfate
Cyanoethoxylation	Silicone Amine
Carboxylation of Silicone Amine	Silicone Amphoteric
Silicone Amination	Silicone Amine Oxide

Table 5. Comparison of hydrocarbon and silicone derivatives

Type	Traditional Products	Silicone Products
Anionic	Phosphate Esters	Silicone Phosphate Esters[3]
Anionic	Sulfates	Silicone Sulfates[4]
Anionic	Carboxylates	Silicone Carboxylates[5]
Anionic	Sulfosuccinates	Silicone Sulfosuccinate[6,7]
Cationic	Alkyl Quats	Silicone Alkyl Quats[8]
Cationic	Amido Quats	Silicone Amido Quats[9]
Cationic	Imidazoline Quats	Silicone Imidazoline Quat[10]
Amphoteric	Aminopropionates	Silicone Amphoterics[11]
Amphoteric	Betaines	Silicone Betaines[12]
Nonionic	Alcohol Alkoxylates	Dimethicone Copolyol
Nonionic	Alkanolamides	Silicone Alkanolamides[13]
Nonionic	Esters	Silicone Esters[14]
Nonionic	Taurine Derivatives	Silicone Taurines[15]
Nonionic	Isethionates	Silicone Isethionates[16]
Nonionic	Alkyl Glycosides	Silicone Glycosides[17]

The emulsions made with J208-612, J208-412 and J208-212 all gave good emulsions. The J208-812 formed a very grainy-looking product with visible flecks of petrolatum. Consequently, it appears that the higher HLB material is not suitable to forming good emulsions with petrolatum.

Because the water:petrolatum ratios are close to equal, the nature of the emulsion (invert or regular) is affected by choice of emulsifier. Clearly, the product made with J208-612 is an invert emulsion, and the product made with J208-212 is a regular emulsion. The product made with the J208-412 has some properties of both.

Derivatization

The final unit operation to consider is derivatization. In this step, reactive groups added in the functionalization step are reacted further to give new compounds. An example is the reaction of a hydroxyl group on a dimethicone copolyol. A variety of reactions have been carried out on dimethicone copolyol. The reactions are shown in **Table 4**.

In fact a series of surface active silicones that parallel the world of standard surfactants has been created and sold commercially. They are identified in **Table 5**.

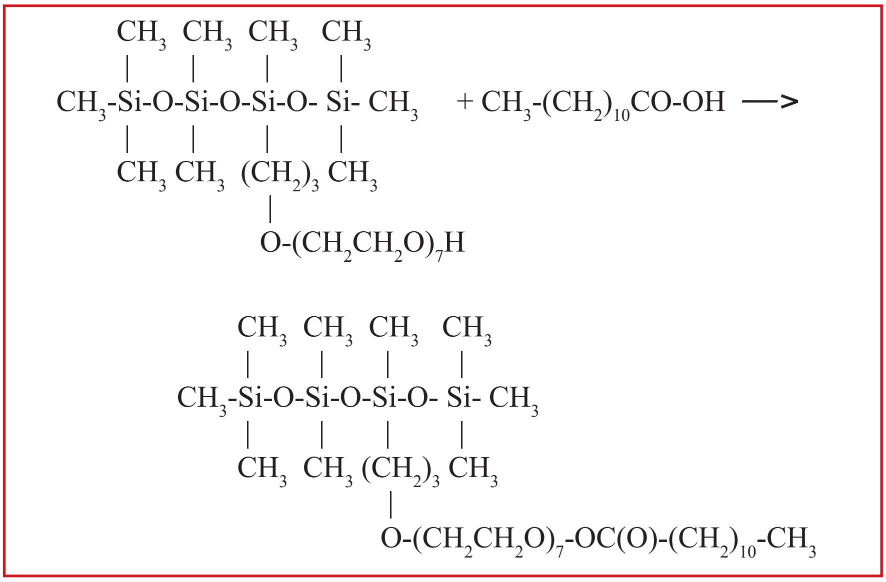
Silicone esters: Silicone esters are a good example of the effect of derivatization upon silicone performance. They are prepared by the esterification reaction of a dimethicone copolyol with a fatty acid. Incorporation of the fatty group by the esterification reaction results in a product that has a water-soluble, a silicone-soluble and a fatty-soluble group present in the same molecule. The reaction is shown in **Figure 11**.

Properties of dimethicone copolyol esters: Dimethicone copolyol esters have the following general properties:

- Compounds with fewer than 12 carbon atoms in the fatty group are liquids at room temperature.
- Saturated linear compounds with more than 14 carbon atoms in the fatty group are solids at room temperature.
- Compounds in which the fatty group is unsaturated or branched are liquids at room temperature.
- The most hydrophobic products have more than 16 carbon atoms in their fatty group.
- The greatest spreadability and lubrication is obtained from the liquid iso-stearic esters.
- Selection of the fatty group is extremely important in determining the solubility of the compound in many organic solvents.
- All products are soluble in lower molecular weight alcohols, such as isopropanol.

Conclusion

Formulating with silicone products can be a source of great joy or great frustration to the formulator and will depend on the degree to which the for-



$$\begin{array}{ccccccccc}
 & CH_3 & & CH_3 & & CH_3 & & CH_3 & \\
 & | & & | & & | & & | & \\
CH_3\text{-} & Si & \text{-O-} & Si & \text{-O-} & Si & \text{-O-} & Si & \text{-}CH_3 \quad + CH_3\text{-}(CH_2)_{10}CO\text{-}OH \longrightarrow \\
 & | & & | & & | & & | & \\
 & CH_3 & & CH_3 & & (CH_2)_3 & & CH_3 & \\
 & & & & & | & & & \\
 & & & & & \text{O-}(CH_2CH_2O)_7H & & &
\end{array}$$

$$\begin{array}{ccccccccc}
 & CH_3 & & CH_3 & & CH_3 & & CH_3 & \\
 & | & & | & & | & & | & \\
CH_3\text{-} & Si & \text{-O-} & Si & \text{-O-} & Si & \text{-O-} & Si & \text{-}CH_3 \\
 & | & & | & & | & & | & \\
 & CH_3 & & CH_3 & & (CH_2)_3 & & CH_3 & \\
 & & & & & | & & & \\
 & & & & & \text{O-}(CH_2CH_2O)_7\text{-OC(O)-}(CH_2)_{10}\text{-}CH_3 & & &
\end{array}$$

Figure 11. Esterification reaction of dimethicone copolyol with a fatty acid to produce a silicone ester

mulator understands the construction, functionalization and derivatization of the molecules used in the formulation. As less and less time is given to develop new products, this understanding becomes even more critical. It is important to develop an understanding of silicone chemistry to formulate successfully.

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